

Mechanistic aspects of microparticle systems

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Editor's Note: The following is an excerpt from the TAPPI Press book *Micro and Nano Particles in Papermaking*, edited by J.M. Rodriguez. Written by leading experts in the industry and academia, the book's nine sections cover topics including drainage and retention, colloidal silica, and clay minerals.

This text has been excerpted from Chapter 1, Microparticle Programs for Drainage and Retention. Only figures, tables and references cited in the portion of the text printed here have been included in this excerpt; the original numbering of figures and text citations for the complete chapter has been preserved to avoid error. **The complete, 207-page book is available through TAPPI Press (Product Code 0101R312) at www.tappi.org.**

Uses of specific microparticle programs and applications will be considered [in the following chapters of the TAPPI Press book], but there seem to be some common features with respect to "how these programs work." This section will consider mechanistic aspects of microparticle programs in general, weighing evidence for and against various concepts. In principle, an understanding of the mechanisms may make it easier to optimize and control additive flows in a microparticle system. Also there may be clues in the mechanisms that can lead to future developments.

Electrostatic effects

Even before the emergence of microparticle programs there has been a lively debate over how significant a role is played by surface charges and zeta potentials with respect to retention and drainage phenomena [166-167]. On the one hand, it has been relatively easy to show a dominant effect of surface charges when one is using a high-charge cationic additive such as a polyamine, polyethylenimine (PEI), or alum [33,152,168-169]. Maximum drainage, and even maximum retention are often associated with an addition rate that achieves an average zeta potential near to zero. This is not necessarily so when one is dealing mainly with high-mass flocculants [168]. Apparently, charge neutralization can be much less important in some cases where very long polymer chains are able to bridge between adjacent surfaces.

So how do microparticle programs fit into this debate, if at all? Microparticle systems seem to be profoundly affected by charge [2,58,61,98,170]. For example, a charge-dependent mechanism helps to explain why the effectiveness of microparticles for drainage promotion seems to increase with increasing surface area (or decreasing size of the primary particles) [2,20]. In cases where the issue has been studied, optimum performance of microparticle programs has approximately coincided with a neutralization of colloidal charges [2,171]. Also, in agreement with classical theories of charge-dependent coagulation, it has been found that increasing salt addition tends to broaden the range of additive ratios over which a maximum interaction can be obtained between a cationic polymer and a microparticle [19]. Often it has been found that excess dissolved polymeric or colloidal anionic materials need to be neutralized with alum or high-charge cationic polymers before a microparticle program can be effective [2,11,23,127,161], or the charge density of the cationic flocculant [79,85] or its dosage [95] has to be increased.

To make matters a bit more complicated, fiber flocculation studies suggest that charge may dominate interactions involving small colloidal silica particles, but that interactions involving the larger bentonite particles may be less charge-dependent [172]. In one study charge issues tended to dominate interactions

between a highly charged cationic polymer and colloidal silica, but different results were obtained when the pH was raised to reduce the effective charge density of the polymer [108]. Similar results were achieved in a related study in which the charge density of the cationic flocculant was varied by chemical composition [173].

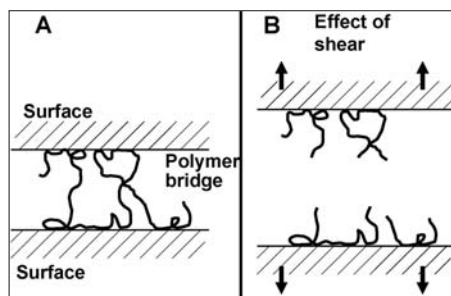
A "drawbridge" concept

The concept of polymeric bridging is already well established as a mechanism of flocculation by polymers [174], but evidence suggests that microparticles form bridges of a different nature. Differences show up in various studies focusing on such aspects as shear resistance, particle size, particle structure, and reversibility of flocculation after redispersal by strong hydrodynamic shear forces. To help distinguish these differences, the word "drawbridge" will be used in this chapter to designate systems in which microparticles help in the process of flocculating systems that already have been treated by a high-mass polymer, and the word "bridging" will be used for systems in which there is no additive that plays the role of microparticle.

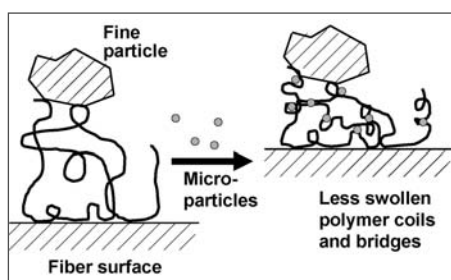
According to Ford [127], if a retention aid is added ahead of a pressure screen, then one can expect hydrodynamic shear to detach some fines from fibers, but others will stay attached to fibers. This situation follows from the observation that higher shear stress is required for detachment of fine particles, compared to that required to detach fibers or larger particles [175-177]. The word "supercoagulation" was coined to describe how the detached fines could be reflocculated upon addition of a microparticle such as bentonite [127]. The combined effects of the surviving polymer bridges and the drawbridges formed with the help of the microparticles can, in one sense, reverse some of the disruption caused by shear.

These two types of bridges are contrasted in **Figs. 2 and 3**. As shown in Fig. 2, breakage of an ordinary bridge is expected to be at least partly irreversible. In other words, breakage of the initial bridges is expected to harm the ability of the polyelectrolytes to function again as flocculating agents.

A more critical mechanistic question involves how the resulting flocs respond to shear after all components of a microparticle system have been added. A microparticle system ought to be considered somewhat reversible if, after being disrupted by hydrodynamic shear, the fibers come together again to a greater extent than they would have in the absence of treatment [178-179]. Such an outcome would



2. Schematic illustration of how the molecular mass of flocculating polymer may decrease when bridges are broken in the presence of hydrodynamic shear.

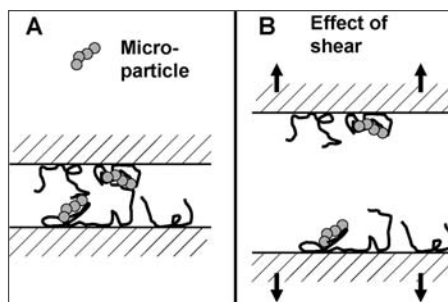


5. Schematic illustration of proposed deswelling mechanism when small microparticles interact with existing polymer bridges or adsorbed polymer.

be consistent with the idealized mechanism illustrated in Fig. 3. At least one study failed to find greater reversibility when microparticle programs were compared to cationic flocculant treatment alone [163]. The idea that flocs formed by microparticle programs have relatively high “reversibility” has been verified [60,171,178], though after sufficiently high shear even microparticle programs may fail to show high levels of reversibility [171].

It has been suggested that reversibility of microparticle-induced drawbridges can promote formation of a porous sheet and good fines retention due to sticking collisions when the fibers ultimately come together on the forming fabric or fabrics [16]. It is worth noting that this is essentially the same mechanism that has been used to explain why unstable colloidal suspensions form sediments of low packing density [180].

Some, but not all investigators have presented evidence that drawbridges formed by microparticle programs are more shear-resistant than those initially formed by a cationic acrylamide copolymer earlier in the same operation. For instance Alfano and coworkers [159]

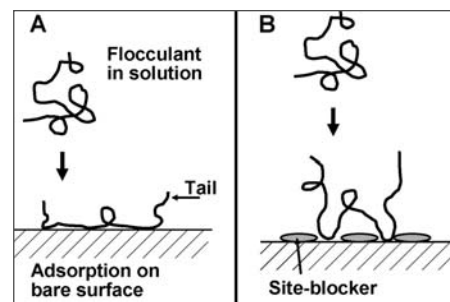


3. Schematic illustration of how unbreakable microparticles can function in a reversible “drawbridge” mechanism of flocculation.

reported that treatment with cPAM alone yielded fiber flocs that decayed rapidly with shear. Subsequent addition of colloidal silica yielded “shear-resistant” flocs, having a slower relative rate of decay of flocculation during continuous agitation. By contrast, some others have reported that the microparticle-induced flocs break down more easily in the presence of shear [22], or noted similar shear-resistance [171-172]. Differences in experimental methods may account for some of the apparent disagreement of the results.

Effect of shear on the bridging flocculants: If one follows a typical microparticle application through the process, the polymeric bridges formed by a cationic starch or cPAM flocculant are partly broken as the stock passes through a pressure screen [6,42,45]. As was illustrated schematically in Fig. 2, such treatment can be expected to reduce the flocculant’s molecular mass before the microparticles are added [181-182]. It may be assumed that the rupture of polymeric bridges can leave a preponderance of “tails” of polymers extending from the adjacent surfaces. Work already described involving highly branched cationic polymers suggests that such a situation may be advantageous for microparticle applications [37]; however, more study is needed to clarify this part of the mechanism.

Size effects: A drawbridge mechanism also is consistent with an observed increase in flocculation effectiveness or increased first-pass retention effects with increasing particle size of microparticles [2,183]. Below a critical size of about 3 to 5 nm, silica microparticles yielded less flocculation in the presence of cationic starch [2]. Montmorillonite, due to its high width to thickness ratio, would be expected to have a high bridging tendency. Consistent with this expectation, Mueller *et al.* [184] found that the poly-



4. Illustration of how partial coverage of fibers with high-charge cationic polymer may cause cationic flocculant molecules to adopt a more extended adsorbed conformation.

meric flocculants had a dominant effect on the extent of flocculation in most of the microparticle systems they tested with colloidal silica, whereas the microparticle had a dominant effect on flocculation whenever a cationic acrylamide copolymer was followed by bentonite. Both optical and rheological studies also revealed strong fiber flocs resulting from bentonite addition to stock pretreated with cationic flocculant [185].

Molecular-mass dependency: Ordinarily one expects that polymer bridging effects should be strongly dependent on polyelectrolyte molecular mass [186]. Recent work by Burgess *et al.* confirmed this expectation, but only in the absence of microparticles [187]. In systems to which microparticles were added there was a greater relative effect of charge densities. One reason to expect higher-mass cationic polyelectrolytes to be more effective is that it takes longer for them to adopt a flat adsorbed conformation; within the short time periods associated with the paper forming process it is expected that loops and tails of very long cationic flocculant molecules remain extended out from the surfaces of solids in a papermaking furnish [36]. Evidence in favor of this mechanism includes a reported benefit of furnish pretreatment with high-charge cationic additives [11,36,129,188]. Though part of the benefit of high-charge cationics might be attributable to neutralization of excess polymeric and colloidal anionic materials [2,11,127,161], the idea here is that partial coverage of surfaces makes it more difficult for a high-mass cationic flocculant to lie down even if there are still sufficient anionic sites remaining for adsorption to take place. Such a “site-blocking” mechanism is illustrated in Fig. 4.

OPTIMIZATION OF A TYPICAL MICROPARTICLE PROGRAM		
Step in Additive Program	Reason for Step	Control Strategies
1. Pretreat furnish with a high-charge cationic additive.	Avoid neutralization of a cationic flocculant and/or partly block surface sites.	Monitor dissolved and colloidal anionic substances by charge titration.
2. Add high-mass cationic flocculant.	Promote retention and provide sites for microparticle attachment.	• Dosage (tray solids test) • Molecular mass • Charge density
3. Apply hydrodynamic shear.	Break fiber-to-fiber flocs for uniform formation and good vacuum dewatering.	Select flocculant addition point, usually before screens or before fan pump.
4. Add microparticle.	Promote water release and compensate for bad effect of shear on fines retention.	• Dosage • Particle type

II. List of some basic steps of a typical (but not universal) microparticle program. As shown, each of the steps can involve some sort of optimization.

Relative affinities: The order of addition of microparticles and other additives ought to make a profound difference, according to fundamental work carried out by Åsselman and coworkers [158,189-190]. Coagulation rate studies showed that montmorillonite formed very strong bonds with chains of cationic polymers extending from fiber surfaces. However, the opposite approach did not appear to work well. Addition of the cationic acrylamide copolymers first to the montmorillonite did not allow it later to adhere well to cellulose. Results were interpreted in terms of a high affinity of the polymer for the highly anionic mineral surfaces, causing the polymer chains to lie down flat. The conventional approach of adding cationic polymer to first to fiber is believed to give a greater likelihood that tails of polymer remain extended from the surface. Related work, using simplified collision-rate calculations [36], supports an assumption that cationic flocculant molecules adsorb very rapidly onto fiber surfaces, but that such polymers then are likely to redistribute partly onto energetically preferred adsorption sites on filler or bentonite particles [191].

Three-dimensional "structure" required?: A question that needs fundamental study is why there seems to be a special advantage in the use of either flocculants or microparticles having a branched structure. It is worth noting that the original silica-based technology involved cationic potato starch, a product that has a high content of branched amylopectin molecules, and that these interacted with non-structured colloidal silica sol particles [3,83]. By contrast, some more recent recipes use linear cationic acrylamide copolymers, but these are paired with "structured" colloidal silica products (gels) in which the primary particles are joined together in chains or clusters [2-3,117]. It has been suggested that three-dimensional microparticles should be an advantage, since they cannot lie flat against a fiber surface, and hence they remain more effective for bridging between the microscopically rough surfaces of fibers [38].

The demonstrated high effectiveness of anionic "filamentary microneutralizer" or "molecular sieve" polymers in the role of microparticles [56] proves that the microparticle need not be solid. It is worth noting that solid latex particles of related composition yielded similar effects [90]. It has been suggested that, to be effective after application of shear, the microparticle must have a solid-like three-dimensional nature and an ability to avoid being torn apart when adjacent polymer bridges are broken [16,56,71].

De-swelling of adsorbed polyelectrolyte coils: Previous work suggests that swollen polymers, including hemicellulose, can offer significant resistance to the dewatering process, and it is unclear whether conventional, high-charge cationic drainage aids can reduce the swelling of these hydrogels [34,169]. Swollen coils of cationic starch or other retention aid polymers are thought have the same effect. As illustrated in **Fig. 5**, the very small size of microparticles, especially in the case of colloidal silica, suggests that these materials are able to penetrate into the coiled structure of adsorbed cationic starch or acrylamide copolymers [2]. Then, one might assume, the complexes formed between the polymer coils and the microparticle would cause the material to contract and expel water [11]. Though this explanation is consistent with increased dewatering and higher wet-press solids [21,25-26,28,39,75,92], it is more difficult to obtain direct evidence. One piece of supporting evidence for this mechanism is an increased density of polymer-induced flocs in fiber-free particulate systems after addition of microparticles [19,187]. There is a need, however, for more direct measurement and quantification of this effect.

OPTIMIZATION AND CONTROL

Today's papermakers who are implementing microparticle programs have a great advantage over the pioneers who made the first attempts in the early 1980's. First, they have the knowledge that many others have been successful [10-13,23]. Second, the pioneers have cleared useful paths and left some helpful hints. While other chapters in this book will go into more detail about specific microparticle program applications, emphasis here will be on some strategies that appear to work in general over a range of microparticle types.

Step 1: Referring to Step 1 of **Table 2**, the usual recommended strategy is to add just enough of the highly cationic material to neutralize most of the anionic colloidal material, while still leaving sufficient anionic sites on the fiber surface so that a cationic flocculant can adsorb efficiently. Spence [192] described a way to determine this optimum dosage level by using a special streaming current titration procedure. For routine testing and for online monitoring it is more usual to directly titrate the white water or filtrate from the headbox to a streaming current reading of zero [193-194]. More stable operations are expected if the cationic demand prior to flocculant

addition is kept at a selected target value [88]. Fiber-pad streaming potential tests seem to be the next most promising type of online sensing method for charge [22,57,195], but most papermakers are still relatively unfamiliar with such methods.

Step 2: When one wants to control the overall retention response of a microparticle system, it is most common to adjust the dosage of the high-mass flocculant [15,67]. In practice this is best achieved with online monitoring and control of tray-water solids [24,88,93]. A possible alternative approach involves online floc size monitoring, especially if there is a good correlation between a floc index and retention [159]. Typical dosage levels of cationic acrylamide copolymers are expected to be in the range of about 0.05 to 0.1% on a solids basis [23].

Step 3: About the only way that papermakers can practically adjust the level of hydrodynamic shear after flocculant addition is to select the addition point. On a typical paper machine there are relatively few options to choose between. The most common choice is just ahead of a pressure screen or screens [6]. Post-screen addition strategies risk an excessive level of fiber flocs in the product, though some of these flocs can be broken as stock passes through a hydraulic headbox [46]. Addition of flocculant at an earlier stage of the process can make sense on relatively slow paper machines [21].

Step 4: Though microparticle dosage clearly is important, it is a common practice to leave the flow of microparticle at a constant level during a production cycle [15]. This approach tends to simplify the control strategy. On the other hand, once excess colloidal charge has been controlled, there is usually an optimum ratio of the flocculant and microparticle [20,172]. More sophisticated control strategies are likely to become commonly used in the future.

Charge balance and addition rates: Charge considerations have been found to be critical for establishing the most effective relative amounts of cationic and anionic components of a microparticle system [2,6,14,22,79,172]. In many cases it has been found necessary to optimize neutralization of excess anionic dissolved and colloidal substances, using such additives as alum or polyaluminum chloride (PAC) [23,25,99], polyamines [10], or high-charge cationic starch [79,154]. In fact, it has been suggested that best results can be achieved if the net amount of cationic polymers is something of an overdose, reversing the original zeta potential [22]. Due to these requirements, one should expect a higher overall requirement of cationic polymers compared to a typical retention and drainage program that does not use microparticles [190]. These considerations tend to make microparticle systems somewhat more expensive and dependent on process sensors and adjustments to keep them working well. In return for these efforts, microparticle systems also appear to be somewhat more tolerant of increased salt levels, compared to conventional retention aid systems [14].

Selection of microparticle type and shape: By selecting a microparticle with larger size or more chaining or agglomeration of primary particles it is possible to shift the benefits more toward retention efficiency and away from an exclusive concentration on drainage and formation [2]. Faster paper machines and twin-wire machines may call for the use of higher-mass, higher-branched flocculant polymers and/or structured microparticles [35].

TRENDS AND NEEDS FOR THE FUTURE

Twenty years ago few papermakers could foresee the upcoming growth and impact of microparticle technology. In retrospect, the developments have come in response to needs for increased production rate and quality. So, one of the first places to look, in asking about the future of microparticles, is at the present needs of papermakers. According to Main [11], advances in paper machine design are tending to decrease the importance of drainage promotion. Rather, the high hydrodynamic shear of modern hydraulic headboxes and twin-wire formers place more critical requirements on achieving acceptable first-pass retention while still maintaining good formation [128].

Strength: Another future emphasis is likely to be on paper strength. Users of low-quality, low-freeness waste paper can use microparticle treatment strategies both as a way of achieving acceptable drainage and as a way of increasing the practical amount of wet-end cationic starch [75]. It is ironic that the earliest technology resembling a modern microparticle system was described as a binder system [107], and that a similar emphasis might again predominate in the future.

Lab test development: Every long-term papermaker will have heard the phrase "you can't observe these benefits in lab tests; you have to run it on the machine to see the benefits." Indeed, conventional freeness tests, etc. sometimes fail to show the benefits of a microparticle program [96]. Due to a lack of water recirculation in some common lab methods it may be necessary to add 4 to 5 times the usual dosage of some additives [85]. To help minimize the lost production and expense of mill trials, there is a need for dynamic tests that better emulate the conditions of shear, pulsating flows, and vacuum application that are inherent in paper forming processes [10]. Much progress already has been achieved [162,196-197]. However, evaluation of microparticle programs, especially at the mill, could benefit from further advances in lab testing. **TJ**

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LITERATURE CITED

- Andersson, K. and Lindgren, E. "Important Properties of Colloidal Silica in Microparticulate Systems," *Nordic Pulp Paper Res. J.* 11(1): 15(1996).
- Harms, M., "Second Generation Microparticle Systems," *Wochenbl. Papierfabr.* 126(19): 922(1998).
- Langley, J.G. and Litchfield, E., "Dewatering Aids for Paper Applications," *Proc. TAPPI 1986 Papermakers Conf.*, 89(1986).
- Cauley, T.A., "The Hydrocol Microparticle System Comes to Standard News Production," *Proc. TAPPI 2000 Papermakers Conf. Trade Fair*, 545(2000).
- Main, S., and Simonson, P., "Retention Aids for High-Speed Paper Machines," *TAPPI J.* 82(4): 78(1999).
- Anon., "Micropolymer Delivers Macro Benefits," *PIMA* 78(3), Advanced Technology II: ATII 18(1996).
- Vaughan, C.W., Adamsky, F.A., and Richardson, P.F., "New Approach to Wet End Drainage/Retention/Formation Technology and its Improvement of Paper Machine Production Rates and Runnability," *Wochenbl. Papierfabr.* 126(10): 458(1998).
- Andersson, K., Sandström, A., Ström, K., and Barla, P., "The Use of Cationic Starch and Colloidal Silica to Improve the Drainage Characteristics of Kraft Pulps," *Nordic Pulp Paper*

- Res. J. 1(2): 26(1986).
15. Wernäs, B., and Litchfield, T., "Microparticle Flocculation Gaining Ground," *Svensk Papperstidn.* 90(15): 18(1987).
16. Lindström, T., "Some Fundamental Chemical Aspects on Paper Forming," in *Fundamentals of Papermaking*, Trans. 9th Fund. Res. Symp., Cambridge, C.F. Baker and V.W. Punton, Eds., Mech. Eng. Publ., Ltd., London, 311(1989).
19. Carlson, U., "Some Aspects of Microparticle Flocculation," *Proc. EUCEPA XXIV: The World Pulp and Paper Week, Paper Technol.*, Stockholm, 161, May 1990.
20. Gill, R.I.S., "Developments in Retention Aid Technology," *Paper Technol.* 32(8): 34(1991).
21. McCourt, A.M., Ford, P.A., and Cauley, T.A., "A Practical View of Microparticle System in Supercalendered Paper," *Tappi J.* 77(10): 165(1993).
22. Penniman, J.G., and Makhonin, A.G., "Optimizing Microparticulate Process Efficiency," *Proc. TAPPI 1993 Papermakers Conf.*, 129(1993).
23. O'Brien, J.A., Lawrence, L.A., and Honig, D.S., "Making Highly Filled Alkaline Paper with a Micropolymer System," *Proc. TAPPI 1994 Papermakers Conf.*, 257(1994).
24. Breese, J., "Interactive Papermaking Chemistry Provides Machine Rebuild Options," *Pulp Paper* 68(4): 91(1994).
25. Hoffmann, J., "Microparticle Systems – Mechanism and Application," *Wochenbl. Papierfabr.* 122(20): 785(1994).
26. Litchfield, E., "Dewatering Aids for Paper Applications," *Appita* 47(1): 62(1994).
28. Swerin, A., Glad-Nordmark, G., and Sjödin, U., "Silica Based Microparticulate Retention Aid Systems," *Paperi Puu* 77(4): 215(1995).
33. Allen, L.H., and Yaraskavitch, I.M., "Effects of Retention and Drainage Aids on Paper Machine Drainage: A Review," *Tappi J.* 74(7): 79(1991).
34. Gruber, E., Gelbrich, M., and Schempp, W., "Morphological and Chemical Effects on Drainage," *Wochbl. Papierfabr.* 125(2): 66(1997).
35. Aloi, F.G., and Trksak, R.M., "Retention in Neutral and Alkaline Papermaking," in J.M. Gess, Ed., *Retention of Fines and Fillers during Papermaking*, TAPPI Press, 1998, 61, see esp. pp. 80-97.
36. Swerin, A., Ödberg, L., and Wågberg, L., "An Extended Model for the Estimation of Flocculation Efficiency Factors in Multicomponent Flocculation Systems," *Colloids Surf.* 113(1/2): 25(1996).
37. Shin, J., Han, S., Sohn, C., Ow, S., and Mah, S., "Highly Branched Cationic Polyelectrolytes: Filler Flocculation," *Tappi J.* 80(11): 179(1997).
38. Wågberg, L., and Nygren, I., "Use of Stagnation Point Adsorption Reflectometry to Study Molecular Interactions Relevant to Papermaking Chemistry," *Colloids Surf. A* 159(1): 3(1999).
39. Lindström, T., "Microparticle Technology – New Megatrend," *Svensk Papperstidn.* 90(1): 24(1987).
42. Chung, D.K., "Retention and Drainage Aid for Alkaline Fine Papermaking Process," U.S. Pat. 5,126,014, June 30, 1992.
45. Cauley, T.A., Langley, J.G., and Nixon, A., "Production of Paper," U.S. Pat. 5,514,249, Jul. 6, 1994.
46. Kiviranta, A., and Paulapuro, H., "Hydraulic and Rectifier Roll Headboxes in Boardmaking," *Paper Technol.* 31(11): 34(1990).
56. Honig, D.S., Harris, E.W., Pawlowska, L.M., O'Toole, M.P., and Jackson, L.A., "Formation Improvements with Water-Soluble Micropolymer Systems," *Tappi J.* 76(9): 135(1993).
57. Miyaniishi, T., and Shigeru, M., "Optimizing Flocculation and Drainage for Microparticle Systems by Controlling Zeta Potential," *Tappi J.* 80(1): 262(1997).
58. Honig, D.S., Turnbull, R.J., and Wheeler, C., "Retention Systems for Highly Filled Paper," *TAPPI 99 Proc.*, 1335(1999).
60. Swerin, A., and Ödberg, L., "Flocculation of Cellulosic Fiber Suspensions by a Microparticulate Retention Aid System Consisting of Cationic Polyacrylamide and Anionic Montmorillonite: Effect of Contact Time, Shear Level, and Electrolyte Concentration," *Nordic Pulp Paper Res. J.* 11(1): 22(1996).
61. Swerin, A., Risinger, G., and Ödberg, L., "Flocculation in Suspensions of Microcrystalline Cellulose by Microparticle Retention-Aid Systems," *J. Pulp Paper Sci.* 23(8): J374(1997).
67. Anon., "Hydrocol for Effective Retention," *Svensk Papperstidn.* 90(1): 39(1987).
71. Nobel, J., and Borgkvist, M., "A New Microparticle-Based Retention Aid System for Alkaline Papermaking. Hydrosil," *Proc. EUCEPA Symp. Additives, Pigments, and Fillers Pulp and Paper Industry (Barcelona)*, 295-306, Oct. 22-24, 1990.
75. Nilsson, L., and Carlson, U., "Improvements in the Production of boards with a Silica Microparticle System Approach," *Proc. TAPPI 1993 Papermakers Conf.*, 181(1993).
79. Fitzgibbons, N., "Retention Management and its Impact on Paper Machine Efficiency," *Proc. TAPPI 1994 Papermakers Conf.*, 237(1994).
83. On, C., and Thorn, I., "Progress in the Use of Colloidal Silica in Dual-Component Systems," *Eur. Papermaker* 3(2): 28(1995).
85. Persson, M., Pal, A., and Wikstrom, O., "High Cationic Starch and Microparticles for Furnish Systems with High Levels of Disturbing Substances," *Proc. 5th Intl. Conf. New Avail. Techniques, 2: World Pulp paper Week*, 567(1996).
88. Tomney, T., Pruszyński, P., Armstrong, J.R., and Hurley, R., "Controlling Filler Retention in Mechanical Grades," *Proc. 1997 Ann. Tech. Mtg. CPPA*, 83rd, B367, (see "additional slides") Jan. 30, 1997.
90. Honig, D.S., Farinato, R.S., and Jackson, L.A., "Design and Development of the Micropolymer System: An 'Organic Microparticle' Retention/Drainage System," *Nordic Pulp Paper Res. J.* 15(5): 536(2000).
92. Reed, R., "Pulp Dewatering Process," U.S. Pat. 4,969,976, Nov. 13, 1990.
93. Bernier, J.-F., and Begin, B., "Experience of a Microparticle Retention Aid System," *Tappi J.* 77(11): 217(1994).
95. Juntai, L., "Cationic Polyacrylamide as a Drainage Aid in Mechanical Pulp," *Tappi J.* 78(4): 149(1995).
96. Adamsky, F.A., and Williams, B.J., "Effects of New Drainage, Retention, and Formation Technology for Improving Production Rates and Runnability of Recycled Fiber Cylinder Machines," *TAPPI J.* 79(8): 175(1996).
98. Vannerberg, N.-G., "The Importance of YKl's Support to Eka Nobel," *1992 Annual Report*, Ytkemiska Institutet, Stockholm, 1992.
99. Moffett, R.H., "Achieving Improved Paper Formation by Use of Polysilicate Microgel," U.S. Pat. 5,584,966, 17 Dec. 1996.
107. Bodendorf, W.J., and Osborne, F.H., "Method of Forming an Inorganic Water-Laid Sheet Containing Colloidal Silica and Cationic Starch," U.S. Pat. 3,253,978, May 31, 1966.
108. Lindquist, G.M., and Stratton, R.A., "Role of Polyelectrolyte Charge Density and Molecular Weight on the Adsorption and Flocculation of Colloidal Silica with Polyethylenimine," *J. Colloid Interface Sci.* 55(1): 45(1976).
117. Andersson, P., *Retention Technologies for Filler-Containing Paper and Board*, EKA Chemicals, 155-174(1998).
127. Ford, P.A., "Control the Wet End Balancing Act with Polymer/Pigment Microparticles," *Proc. TAPPI 1991 Papermakers Conf.*, 501, (1991).

128. Swerin, A., and Mähler, A., "Formation, Retention, and Drainage of a Fine Paper Stock During Twin-Wire Roll-Blade Forming. Implications of Fiber Network Strength," *Nordic Pulp Paper Res. J.* 11(1): 36(1996).
129. Wågberg, L., Björklund, M., Åsell, I., and Swerin, A., "On the Mechanism of Flocculation by Microparticle Retention-Aid System," *TAPPI J.* 79(6): 157(1996).
152. Brouwer, P., Johnson, M., and Olsen, R., "Starch and Retention," in *Retention of Fines and Fillers During Papermaking*, J. Gess, Ed., TAPPI Press, Atlanta, Ch. 10, 199(1998).
154. Au, C.O., and Johansson, K.A., "Use of Cationic Starch and Anionic Colloidal Silica in Waste," *Pulp Paper Can* 94(6): 55(1993).
158. Dugal, H.S., and Swanson, J.W., "Effect of Polymer Mannan Content on the Effectiveness of Modified Guar Gum as a Beater Adhesive," *Tappi* 55(9): 1362(1972).
159. Alfano, J.C., Carter, P.W., and Whitten, J.E., "Use of Scanning Laser Microscopy to Investigate Microparticle Flocculation Performance," *J. Pulp Paper Sci.* 25(6): 189(1999).
161. Johansson, H.E., "Process for the Production of Paper," U.S. Pat. 4,964,954, Oct. 23, 1990.
162. Najaranan, R., and Wong Shing, J.B., "Papermaking Process," U.S. Pat. 6,007,679, Dec. 28, 1999.
163. Krogerus, B., "Impact of Retention Polymers on Flocculation, Retention, Drainage, and Sheet Formation. A Laboratory Study," *Proc. TAPPI 1994 Papermakers Conf.*, 445(1994).
166. Davison, R.W., and Cates, R.E., "Electrokinetic Effects in Papermaking Systems: Theory and Practice," *Paper Technol. Ind.* 16(2): 107(1975).
167. Stratton, R.A., and Swanson, J.W., "Electrokinetics in Papermaking: A Position Paper," *Tappi* 64(1): 79(1981).
168. Horn, D., and Melzer, J., "Influence of Macromolecular Cationic Drainage Aids on Electrokinetic Properties," *Papier* 29(12): 534(1975).
169. Ström, G., and Kunas, A., "The Effect of Cationic Polymers on the Water Retention Value of Various Pulps," *Nordic Pulp Paper Res. J.* 6(1): 12(1991).
170. Durand-Piana, G., Lafuma, F., and Audebert, R., "Flocculation and Adsorption Properties of Cationic Polyelectrolytes toward Na-Montmorillonite Dilute Suspensions," *J. Colloid Interface Sci.* 119(2): 474(1987).
171. Hubbe, M.A., "Reversibility of Polymer-Induced Fiber Flocculation by Shear. 2. Multi-Component Chemical Treatments," *Nordic Pulp Paper Res. J.* 16(4): 226(2001).
172. Clemençon, I., and Gerli, A., "Effect of Flocculant/Microparticles Retention Programs on Floc Properties," *Paper Technol.* 41(8): 25(2000).
173. Wang, T.K., and Audebert, R., "Flocculation Mechanisms of a Silica Suspension by Some Weakly Cationic Polyelectrolytes," *J. Colloid Interface Sci.* 119(2): 459(1987).
174. Gregory, J., and Sheiham, I., "Kinetic Aspects of Flocculation by Cationic Polymers," *Br. Polymer J.* 6(1): 47(1974).
175. McKenzie, A.W., "Structure and Properties of Paper. XVIII. The Retention of Wet-End Additives," *Appita* 21(4): 104(1968).
176. Hubbe, M.A., "Detachment of Colloidal Hydrous Oxide Spheres from Flat Solids Exposed to Flow. 2. Mechanism of Release," *Colloids Surf.* 16: 249(1985).
177. Hubbe, M.A., "Retention and Hydrodynamic Shear," *Tappi J.* 69(8): 116(1986).
178. Hedborg, F., and Lindström, T., "Some Aspects on the Reversibility of Flocculation of Paper Stocks," *Nordic Pulp Paper Res. J.* 11(4): 254(1996).
179. Hubbe, M.A., "Reversibility of Polymer-Induced Fiber Flocculation by Shear. 1. Experimental Methods," *Nordic Pulp Paper Res. J.* 15(5): 545(2000).
180. Kline, J.E., "The Application of the Verwey-Overbeek Theory to the Relative Sediment Volume of Kaolin-Water Dispersions," *Tappi* 50(12): 590(1967).
181. Sikora, M.D., "Shear Stability of Flocculated Colloids," *Tappi* 64(11): 97(1981).
182. Tanaka, H., Swerin, A., and Ödberg, L., "Transfer of Cationic Retention Aid from Fibers to Fine Particles and Cleavage of Polymer Chains under Wet-End Papermaking Conditions," *Tappi J.* 76(5): 157(1993).
183. Wall, S., Samuelsson, P., Degerman, G., Skoglund, P., and Samuelsson, A., "The Kinetics of Heteroflocculation in the System Cationic Starch and Colloidal Anionic Silicic Acid," *J. Colloid Interface Sci.* 151(1): 178(1992).
184. Mueller, P., Gruber, E., and Schempp, W., "Investigations of the Flocculation Behavior of Microparticle Retention Systems," *Wochenbl. Papierfabr.* 129(1-2): 36(2001).
185. Swerin, A., Risinger, G., and Ödberg, L., "Shear Strength in Papermaking Suspensions Flocculated by Retention-Aid Systems," *Nordic Pulp Paper Res. J.* 11(1): 30(1996).
186. Durand-Piana, G., Lafuma, F., and Audebert, R., "Flocculation and Adsorption Properties of Cationic Polyelectrolytes toward Na-Montmorillonite Dilute Suspensions," *J. Colloid Interface Sci.* 119(2): 474(1987).
187. Burgess, M.S., Phipps, J.S., and Xiao, H., "Flocculation of PCC Induced by Polymer/Microparticle Systems: Floc Characteristics," *Nordic Pulp Paper Res. J.* 15(5): 572(2000).
188. Wågberg, L., and Eriksson, J., "New Equipment for Detection of Polymer Induced Flocculation of Cellulosic Fibers by Using Image Analysis – Application to Microparticle Systems," *Chem. Eng. J.* 80(1-3): 51(2000).
189. Asselman, T., Alince, B., Garner, G., and Van de Ven, T.G.M., "Mechanism of Polyacrylamide-Bentonite – Microparticulate Retention Aids," *Nordic Pulp Paper Res. J.* 15(5): 515(2000).
190. Asselman, T., and Garnier, G., "The Flocculation Mechanism of Microparticulate Retention Aid Systems," *J. Pulp Paper Sci.* 27(8): 273(2001).
191. Cho, B.-U., Garnier, G., Paradis, J., and Perrier, M., "Filler Retention with a cPAM/Bentonite Retention System – Effect of Collision Efficiency," *Nordic Pulp Paper Res. J.* 16(3): 188(2001).
192. Spence, G.G., "A Titration Procedure for Determining the Level of Anionic Impurities in a Pulp Furnish," *PaperAge* 113(7): 30(1997).
193. Bley, L., "Measuring the Concentration of Anionic Trash – the PCD," *Paper Technol.* 33(4): 32(1992).
194. Chen, J., Hubbe, M.A., and Heitmann, J.A., "Measurement of Colloidal Charge in the Paper Mill by Streaming Current," *Proc. TAPPI 2001 Papermakers Conf.*, 2001.
195. Hubbe, M.A., "Method and Apparatus for Measuring and Electrical Property of Papermaking Furnish," U.S. Pat. 5,936,151, Aug. 10, 1999.
196. Britt, K.W., and Unbehend, J.E., "Water Removal During Paper Formation," *Tappi J.* 68(4): 104(1985).
197. Räisänen, K.O., Paulapuro, H., and Karila, S.J., "The Effects of Retention Aids, Drainage Conditions, and Pretreatment of Slurry on High-Vacuum Dewatering: A Laboratory Study," *Tappi J.* 78(4): 140(1995).